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REPORT

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SOLID STATE HYDROGEN STORAGE
MATERIALS FOR APPLICATION
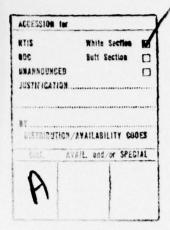TO ENERGY NEEDS

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FINAL TECHNICAL REPORT

SOLID-STATE HYDROGEN STORAGE
MATERIALS FOR APPLICATION TO ENERGY NEEDS

August 1976

- Submitted by -

University of Denver
Denver Research Institute
Denver, Colorado 80210

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Six areas of study of solid state hydrogen storage materials were completed in the two and one half year study. These were (1) literature survey and field trips relating to studies of hydrogen storage materials, (2) safety characteristics of $LaNi_5$ hydrides, (3) general hydriding characteristics of $LaNi_5$, (4) study of kinetics of hydrogen desorption of $LaNi_5$, (5) studies of new alloy systems, and (6) development of fundamental insights of hydriding and of predictive criteria for new and improved hydrides. The safety characteristics of $LaNi_5$ were fully evaluated in terms of the properties of powders. Bulk powder properties

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determined were: ignition temperature, relative combustibility, flammability, shock sensitivity, impact sensitivity, spark sensitivity, and explosibility. Studies of dispersed dust clouds were conducted in which ignition temperature, minimum ignition energy, minimum explosive concentration, maximum explosive pressure, and maximum rate of pressure rise were determined. From these data, an index of explosibility was obtained, which indicated a "weak" rating. The general hydriding characteristics included data on activation, effects of repetitive cycling, hysteresis effects, surface poisoning effects, and more precise pressure-temperature-composition relationships of the system than have been available in the literature. The kinetics of hydrogen desorption from $LaNi_5$ hydride were established. The order, rate constant, and activation energy were determined. The effects of surface contamination were studied by exposure to air, oxygen, and moisture. Evaluation was conducted principally by the change in the kinetics of desorption of hydrogen. Enhancement studies of hydrogen absorption in new systems were carried out to effect two goals; (1) to develop storage materials with improved properties and (2) to establish a more fundamental understanding of the occlusive process which would lead to predictive criteria. As a result, criteria were evolved. A correlation was established between the free energy of formation of the hydrides of hexagonal AB_5 ($CaCu_5$) and cubic AB (CsCl) intermetallic compounds and the size of the interstitial hole in the compounds. The correlation is that the larger the size of the interstitial hole, the more stable is the hydride. The principal find of new hydride materials was that of cerium-free, mischmetal penta-nickel compound which is much less costly, yet has similar properties to $LaNi_5$.

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I.   TECHNICAL REPORT SUMMARY

The general areas of study of solid state, hydrogen storage materials during the two and one half year report period were as follows: (1) safety characteristics of $LaNi_5$ hydrides, (2) general hydriding characteristics of $LaNi_5$, (3) study of the kinetics of hydrogen desorption from $LaNi_5$ hydride, (4) studies seeking enhanced hydrides from new alloy systems, (5) development of fundamental insights of hydriding of various intermetallic compounds, and (6) development of predictive criteria for new and improved "unstable" hydrides.

The safety characteristics of $LaNi_5$ were fully evaluated in terms of the properties of hydride powders. The bulk powder properties were: ignition temperature, relative combustibility, flammability, shock sensitivity, impact sensitivity, spark sensitivity, and explosibility. Studies of dispersed dust clouds were conducted in which ignition temperature, minimum ignition energy, minimum explosive concentration, maximum explosive pressure, and maximum rate of pressure rise were determined. From these data an Index of Explosibility was obtained. The $LaNi_5$ hydride was rated as a "weak" safety hazard.

The general hydriding characteristics determined included the following: (1) minimum activation requirements (2) effects of repetitive cycling on hydriding characteristics and the comminution behavior, (3) hysteresis effects, (4) surface poisoning sensitivity, (5) and precise pressure-temperature-composition relationships of well-characterized $LaNi_5$ from which were deduced and/or calculated solubility boundaries and thermodynamic properties.

The kinetics of hydrogen desorption from $LaNi_5$ hydride were established by careful experimental techniques. The order of the reaction, the rate constant, and the energy of activation were determined. First-cycle desorption data at 25°C yielded second-order-reaction kinetics with a rate constant of

$7.7 \times 10^{-2} \ sec^{-1}(H/LaNi_5)^{-1}$. From an Arrhenius plot over the temperature range, 15 to 25°C, the energy of activation was determined to be -21.9 kcal/mole. Additional surface poisoning effects were determined employing the measurement of kinetics of the contaminated surface compared to a "clean" surface. The kinetics of desorption from surfaces prepared as clean and fresh as possible were found to be extremely sensitive to minor amounts of contamination. On the other hand, the gross exposure of $LaNi_5$ hydride to air, oxygen, and moisture at room temperature and elevated temperatures indicated that the activation, kinetics of desorption, and hydrogen saturation remained surprisingly good.

The studies of the hydriding characteristics of new alloy systems to seek enhanced hydride properties led to achieving two other objectives that were also sought. These were to learn more of the fundamental behavior of the occlusive process in this group of "unstable" hydrides which in turn would allow the development of predictive criteria for the selection of the new alloy systems. Those alloy systems which were studied in this phase of the program included the following; selected alloys in the V-Cr system, selected alloys in the Nb-Mo system, $CeAl_4$, $CeAl_2$, CeAl, CoTi, NiTi, αTi solid solution saturated with Al, $CaCu_5$, $CeCo_5$, $CaNi_5$, HfNi, CeMg, $ZrBe_5$, $La_4Ce_6Ni_5$, $La_2Ce_8Ni_5$, various mischmetal-Ni_5 compounds, $CeNi_5$, selected alloys in the rare earth-Cu_4 and rare earth-Cu_5 systems, selected alloys in the rare earth-Fe_4 and rare earth-Fe_5 systems, $PrNi_5$, $NdNi_5$, $HoNi_5$, and YNi_5.

During the studies of the new systems above, extensive efforts were also underway to analyze the results for correlations of hydriding and/or thermodynamic properties with fundamental properties of the alloy system itself. Out of this study evolved a correlation relating the tetrahedral interstitial hole size in the intermetallic compound to the free energy of formation of

the hydride (at ambient temperature). The free energy of formation is related to the pressure stability of the system through the formula, $\Delta F^\circ = RT \ln p_{H_2}$. The correlation was established with AB_5 ($CaCu_5$ type) systems where A consisted primarily of rare earths and B of nickel or cobalt. Also, a correlation was established with AB (CsCl type) systems, where A consisted of Fe, Co, and Ni and B consisted of Ti. The correlations were very good, and established that as the interstitial hole size of the inter-metallic compound decreases, the free energy of formation of the hydride decreases (the plateau pressure at ambient temperature increases). The cor-relations were made quantitative by plots of the data. The correlations were found to be qualitatively useful also when ternary additions were made to the binary intermetallic compounds to adjust the plateau pressure equilibria. Predictions of the effects based on the size of the solute atom and its effect on the hole size were found to be generally valid.

Of the new systems examined, several were thought to have potential for ternary alloy development. However, the one system with by far the greatest possibilities for commercial application was cerium-free, mischmetal-Ni_5. Pressure-temperature-composition data were obtained along with Van't Hoff data. The alloy has all of the desirable properties of $LaNi_5$ and overcomes the one undesirable feature of $LaNi_5$; that is, cost. The cerium-free misch-metal is essentially equivalent with mischmetal in cost. Mischmetal is about \$3.50 to \$4.00 per pound, whereas La is about \$150 at current day prices.

II.   INTRODUCTION

This Final Technical Report is due under Contract No. F44620-74-C-0020, Air Force Office of Scientific Research, sponsored by the Advanced Research Projects Agency, Department of Defense under ARPA Order No. 2552-1.   The report period is from 1 October 1973 to 31 March 1976.

Generally, the program plan for this contract was to carry on a multi-phase effort to investigate the potential and test the feasibility of employing metallic hydrides to store hydrogen for subsequent power or energy use. The materials under study primarily consisted of binary and ternary metallic systems of both intermediate phases and alloys thereof.   The concept of using such materials as an energy source was explored in terms of several fundamental property characteristics:

1.   Pressure-temperature-composition relationships.

2.   Kinetics of absorption and desorption.

3.   Surface poisoning effects.

4.   Potential safety hazards.

A systematic investigation of the hydriding characteristics of various alloy combinations was also planned to develop better criteria for the prediction of the occurence and extent of hydrogen occlusion in hydrides that may be classified as "unstable" alloy hydrides.   It was anticipated that a better understanding of this class of alloys would emerge.

III.   SAFETY CHARACTERISTICS OF LaNi$_5$ HYDRIDE

A.   INTRODUCTION

Experimental studies were conducted to determine the limits of safety in handling, shipping, and usage of LaNi$_5$ hydride. Emphasis was given to the accident-oriented safety problems such as punctured containers, impact, explosion, shock, and external fire. Although it is presumed this type of hydrogen storage system is relatively safe to handle compared to high-pressure tank hydrogen or liquified hydrogen, the safety characteristics had never been thoroughly assessed. It was the objective of this study to completely analyze the safety characteristics of LaNi$_5$ hydrides.

Various aspects of hazards were evaluated for bulk powders; the ignition temperature, the relative combustibility, flammability, shock sensitivity, and potential explosibility. Since the LaNi$_5$ hydrides break down to powders after repeated absorption and desorption of hydrogen, the ultimate interest in the safety considerations is with fine powders. A characterization study of the particles and particle size was determined. Another independent study was also made of the safety of dust clouds of LaNi$_5$ hydrides. The ignition sensitivity and explosion severity were determined, and an index of explosibility of dust clouds was established.

B.   CHARACTERIZATION OF LaNi$_5$

Both metallographic and x-ray analyses were performed on the original ingot. Metallographic analysis demonstrated that the ingot was homogeneous. Experimentally determined values for the lattice parameters and the density agreed with the published values. A chemical analysis was conducted. The LaNi$_5$ alloy was found to contain 67.61% nickel. The theoretical composition for LaNi$_5$ is 67.88 weight percent. The first

consideration prior to commencing the safety studies and the general hydriding studies was to characterize and understand the physical nature of the hydrided powders. Three portions of hydrided LaNi$_5$ were prepared: one cycle, 10 cycles, and 20 cycles. Most of the size reduction occurs in the first cycle where 99.5% of the material is already less than 74 microns. After that the size of the particles appears to stabilize in spite of the additional number of cycles. The average particle size as determined by the ASTM optical method also demonstrated that there isn't much change in size after the first cycle. The average size was found to be 15 microns after the first cycle, 12 microns after 10 cycles, and 11 microns after 20 cycles.

C. BULK POWDER SAFETY STUDIES .

The definition of bulk powders are those that exist in loose compaction in the bulk due to their own weight as opposed to a dust cloud of powder which is greatly dispersed. All of the powder studies were conducted with LaNi$_5$H$_{6.7}$ that had been hydrided at least through four cycles, so the average particle size was down in the range of 12 microns.

1. Ignition and Combustibility Properties

For reactive metals, a strongly exothermic reaction occurs with the oxygen in air. Ignition of metal powders is the temperature at which the rate of heat generated with the air-surface reaction exceeds the heat loss to the surroundings. The reaction is then carried on autocatalytically, and the powder continues to combust as long as the supply of air is sufficient and the reaction products on the particles are not impenetrable to oxygen.

LaNi$_5$ has a very gentle ignition point and combustion energy. In pure oxygen, LaNi$_5$ is ignited at a lower temperature and with

more energy of combustion compared to $LaNi_5$ in air. In air, the energies of both $LaNi_5$ and $LaNi_5$ hydride are reduced compared to those in oxygen. In general, the hydrides either in air or in oxygen are ignitable at lower temperatures and have greater combustibility. However, compared to a reactive metal like cerium, they are considerably less ignitable and combustible. In no case did the hydrogen desorbing from the hydride react explosively with either air or oxygen in the enclosure. The kinetics of the burning, once ignited, were very slow compared to a reactive metal such as La or Ce.

2. Flammability Studies

Flammability is defined as the combustion properties when a flame is intentionally employed to ignite the hydrogen which is desorbing or emanating from the hydride powder. Three tests were conducted: (1) with a completely open system, (2) with an enclosed system having a partially restricted opening. In all cases, the flammability was accompanied only by gentle burning of the desorbing hydrogen. No explosive reactions occurred.

3. Shock Studies

It is well known that explosives and reactive materials, including mixtures of oxygen and hydrogen (18 to 59 vol. percent), can be sensitive to shock. The standard test in the Department of Defense to characterize explosive sensitivity to shock is the card-gap test [1]. It is used to compare the shock sensitivity of various explosive materials. Basically, it consists of a donor charge set off by an electric cap, a barrier of plastic sheet, the acceptor charge, and a means to detect the degree of explosibility due to

shock. A test of this type was conducted using the LaNi$_5$ hydride as the acceptor. The test was completely negative. No damage was observed in the witness plate. The shock did not even ignite the hydride powder.

4. Impact and Friction Study

Two separate tests were conducted to determine the effect of impact and friction on the LaNi$_5$ hydride powder. These were: the drop test and the bullet test, which again are standard Department of Defense tests for explosives.[1]

The bullet test, which is used for differentiating the sensitivity to frictional impact, was conducted on LaNi$_5$ hydride. It consists of firing a .30 caliber bullet from 30 yards into a container of the material to be tested. Usually a visual test suffices to measure the sensitivity. The ratings are: (1) no effect, (2) emission of smoke, (3) emission of flame, and (4) explosion. In the case of the tested LaNi$_5$ hydride, the test was completely negative.

5. Electrostatic Spark Susceptibility

Electrostatic spark discharges are always prevalent and insidious sources for causing unexpected explosions. A standard test was conducted through the cooperation of the Bureau of Mines[2]. The electrical energy required for the ignition of a layer of powder is determined by discharge of a condenser at 400 volts through a 1/16 in layer. The value obtained for LaNi$_5$ unhydrided was 0.04 joules and that for LaNi$_5$ hydride was 0.16 joules. In other words, it took more energy to ignite the hydride by electrostatic spark. Comparisons with other hydrides showed a relative

insensitivity to ignition by spark of $LaNi_5$ hydride.

6. Dust Explosion Test

The effect of exploding a charge in the center of mass of a
bulk amount of $LaNi_5$ hydride powder was determined at the DRI
ballistics range. A charge of 400 grams of powder was placed in
a plastic container. Imbedded in the center was an electric
blasting cap. The cap was exploded causing the bulk powder to be
dispersed into a dust cloud in the air. The combined effect of
the explosion and heat of the blasting cap was not enough to ignite
the dust cloud.

D. DUST CLOUD SAFETY STUDIES

A dust cloud consists of a levitation of bulk powders into an air
suspension. A dust explosion is a rapid combustion of this cloud where
heat is generated faster than it is dissipated. Many different mater-
ials that are combustible will, when powdered finely enough, explode
on being dispersed in air and ignited. To cause a dust explosion to
occur, one must raise a small portion of the cloud up to its ignition
temperature.

Arrangements were made with the U.S. Bureau of Mines Industrial
Safety Group at their Pittsburgh Technical Support Center, Pittsburgh,
Pa., to determine the Explosibility Index for both $LaNi_5$ and $LaNi_5$ hydride
in powder form.

1. Determination of Ignition Sensitivity

Ignition sensitivity is assumed to be a function of ignition
temperature, minimum ignition temperature, and minimum explosive
concentration. It is defined as unity for a dust similar to Pitts-
burgh seam coal and is calculated as follows:

$$\text{Ignition Sensitivity} = \frac{(\text{Ign. temp. x min. ign. energy x min. conc.}) \text{ Coal Dust}}{(\text{Ign. temp. x min. ign. energy x min. conc.}) \text{ Sample Dust}}$$

2. Determination of Explosion Severity

Explosion severity is assumed to be a function of maximum explosion pressure and rate of pressure rise. Again, it is defined as unity for a dust similar to Pittsburg seam coal and is calculated as follows:

$$\text{Explosion Severity} = \frac{(\text{Max. exp. press. x max. rate of press. rise}) \text{ Sample Dust}}{(\text{Max. exp. press. x max. rate of press. rise}) \text{ Coal Dust}}$$

3. Determination of Index of Explosibility

The Index of Explosibility is measured as follows:

Index of Explosibility = Ignition Sensitivity x Explosion Severity

The Indexes of Explosibility for both $LaNi_5$ and $LaNi_5$ hydride were determined to be 0.1, or a rating of "weak". Vanadium metal is comparable to $LaNi_5$ Hydride. An example of a highly explosive dust is UH_3 which has an Index of Explosibility of 10.

IV.   GENERAL HYDRIDING CHARACTERISTICS OF LaNi$_5$

   A.   INTRODUCTION

   It was the objective in this phase of the program to very accurately
determine the pressure-temperature-composition (PTC) relationships, the
heat of reaction, and other hydriding characteristics of a well-charac-
terized LaNi$_5$ starting material. There was so much variation of the
data in the literature, this objective seemed obligatory. The data
obtained were presented in the First Annual Technical Report[3] and
published in the Proceedings of the IECEC[4]. Both absorption and
desorption data were delineated.

   B.   DETERMINATION OF PRESSURE-TEMPERATURE-COMPOSITION RELATIONSHIPS

   A family of isotherms in both absorption and desorption was deter-
mined at every 10°C interval from 25 to 65°C. The solid solution solu-
bility boundary was placed at about 0.3 H/LaNi$_5$ and the hydride solubility
boundary at 5.8 H/LaNi$_5$. Saturation at 100 atmospheres was placed at
about 6.6 H/LaNi$_5$ at 25°C. The shapes of the isotherms roughly paralleled
each other. Hysteresis effects on absorption versus desorption were con-
sistently observed. The role of the history of the sample was found to
expand or contract the hysteresis. This effect is not yet fully under-
stood, but is thought to be a manifestation of surface chemistry or pos-
sibly bulk strains in the material as it is being hydrided or dehydrided.

   A correlation was made with the investigation of K. H. J. Buschow
and H. H. Van Mal [5] on the dependence of the plateau pressure equilibria
with the composition of the LaNi$_5$ alloy. The Dutch investigators found
a relatively wide homogeneity range of the LaNi$_5$ phase at elevated tem-
peratures. This, in turn, affected the plateau pressure equilibria as
a function of the composition of LaNi$_x$ at any isotherm, where x varied

from 4.9 to 5.4. The correlation was excellent.

The x-ray diffraction lattice parameters were determined for the material in this study and also correlated with those of Buschow and Van Mal.

C. DETERMINATION OF VAN'T HOFF RELATIONSHIPS

This study established the heat of reaction as 7.6 ± 0.1 kcal/mole H_2 being the same for desorption as for absorption. This compares with a value of 7.2 kcal/mole H_2 as reported by van Vucht[6], and 7.3 kcal/mole H_2 as reported by J. Anderson, et al.[7].

D. SURFACE POISONING EFFECTS

Evaluations were carried out on the poisoning effects at the surface of $LaNi_5$ hydrides by various contaminants. The contaminants were water vapor, air, and organic vapor (oil). In no case of exposure was the surface absorption or desorption of hydrogen completely blocked. The rates were only mildly affected throughout the hydriding range of approximately 25 to 65°C. Some effect was noted on the total saturation absorptivity and the reproducibility of the pressure plateaus. In the case of air exposure, tests were conducted to determine whether $LaNi_5$ hydride, reacted to full saturation, would passivate by removal from the hydriding apparatus. The samples continued to desorb at room temperature with rapid kinetics in spite of the complete air exposure. Very little reactivation to initiate hydrogen absorption was required when the $LaNi_5$ was placed back in the pressure hydriding apparatus.

In general, the $LaNi_5$ intermetallic compound demonstrated surprisingly good resistance to surface passivation to hydrogen passage by water vapor, air, or organic vapor contaminants.

V.   STUDY OF THE HYDRIDING KINETICS OF LaNi$_5$

The determination of the kinetics of hydrogen desorption from LaNi$_5$ hydride was an extensive, difficult process complicated by two fundamental material properties; the high reactivity at ambient temperatures and the task of maintaining isothermal conditions due to the endothermic heat of reaction. However, a reactor was designed and employed successfully to obtain hydriding kinetics. First cycle desorption data at 25°C yielded an excellent fit to second-order-reaction kinetics with the rate constant, 7.7 x 10^{-2} sec $^{-1}$ (H/LaNi$_5$)$^{-1}$. Additional desorption cycles showed a gradual deterioration of kinetics. Accumulating surface contamination was the suspected cause of this deterioration.

An Arrhenius plot was prepared of ln k (reaction rate constant) versus reciprocal absolute temperature. The data were taken in the temperature range from 15 to 25°C. The activation energy determined from this plot was -21.9 kcal.

The kinetic apparatus was employed to determine the gross contamination of LaNi$_5$. The susceptibility of LaNi$_5$ to poisoning by air, O$_2$, or H$_2$O at temperatures up to 100°C was found to be only temporary and limited to the kinetic behavior. The ultimate H/LaNi$_5$ saturation value was uneffected if sufficient time was allowed for equilibration.

Details of the equipment and the kinetics of desorption studies can be found in reference 4.

VI. EXPLORATORY STUDIES OF NEW HYDRIDE SYSTEMS

This phase of study was designed to search, select, and screen for alloys that appear to have promise as potential unstable hydrides. The ultimate goal of this program was to develop hydrides that demonstrate excellent storage and retrieval of hydrogen capabilities for subsequent power or energy application. Generally, the properties sought for an ideal storage material were as follows:

1. High saturation capacity for hydrogen

2. Reasonable density of metal or hydride

3. Low heat of reaction

4. Surface passivity to contaminants

5. Rapid kinetics of absorption

6. Near ambient pressure-temperature relationships

7. High thermal conductivity

8. Low heat capacity

9. Ability for indefinite recycling

10. Stable powder size after several cycles

11. Safe materials to handle and use

12. Low cost materials

Obviously, one cannot achieve all of these properties simultaneously in one hydride. However, an adequate compromise should be found compatible with the application, resulting in a material that would be suitable for efficient use, practical operation, and reasonable cost.

The approach taken in this phase was to select promising candidates of both binary and ternary systems based on what was known of hydrides, in general. Various guidelines were employed, however, which should greatly increase the probabilities of selecting and developing new guidelines were as follows:

1. For intermetallic compounds, the selection of structure-types that are compatible with hydriding were chosen.

2. For ternary compositions, a rationale for selection was followed, such as the search for possible pseudo-binary systems for solid solutions of binary intermetallic compounds.

3. Considerations of the valence, the atomic diameter, electron concentration, size of interstices, and electronic structure were taken into account as one would with the stable hydrides.

4. A liberal use of transition metals in Groups III, IV, and V transition metals was sought because of their known propensity to hydrogen occlusion.

5. The avoidance of the surface-active elements because of the possible poisoning activity was stressed.

6. The selection of predominantly brittle materials was made, since microfractrue is felt to be a criterion of optimum kinetics of desorption.

7. Attention was closely paid to the ternary and quaternary phase equilibria in the rationale of selection.

8. Selection was made of elements of the system which are reasonable in cost, although this was not always followed if some fundamental insights could be divulged.

9. The use of elements in the alloy systems with a density of less than about 8.5 grams/cc, was generally followed for the practicality of application.

10. Quaternary addition elements were selected in some cases for possible passivation of the surface to poisons.

11. Intermetallic compounds were chosen so that at least one of the multiple of elements was capable of forming a binary hydride.

12. As the program progressed, the development of the prediction criteria was advancing. These were employed more and more as they evolved, and were ultimately useful in the selection process.

The alloy systems which were studied in this phase of the program included the following; selected solid solution alloys in the V-Cr system, selected solid solution alloys in the Nb-Mo system, $CeAl_4$, $CeAl_2$, $CeAl$, CoTi, NiTi, α-Ti solid solution saturated with Al, $CaCu_5$, $CeCo_5$, $CaNi_5$, HfNi, CeMg, $ZrBe_5$, $La_{.4}Ce_{.6}Ni_5$, $La_{.2}Ce_{.8}Ni_5$, $CeNi_5$, selected compounds in the rare-earth-Cu_4 and rare-earth-Cu_5 systems, selected alloys in the rare-earth-Fe_4 and rare-earth-Fe_5 systems, $PrNi_5$, $NdNi_5$, $HoNi_5$, YNi_5, and various mischmetal $(MM)Ni_5$ samples. The details of many of these systems were reported earlier[3] along with the experimental techniques. The remaining systems will be discussed in this report.

1. $CaCu_5$-H System

This compound activated at room temperature and 90 atm. No PTC data were taken, because the hydride was found to be extremely stable. A Van't Hoff plot was determined. The Van't Hoff relationship was found to be

$$\ln p(atm) = \frac{-14,300}{T} + 15.0$$

The heat of formation of the hydride was determined to be -28.4 kcal/ mole H_2.

2. $CeCo_5$-H System

The compound activated readily at room temperature and 90 atm. The saturated composition was found to be $CeCo_5H_{2.8}$ at 33.5 atm. No PTC data were taken, because the hydrogen saturation was so low. The Van't Hoff relationship was established to be:

$$\ln p(\text{atm}) = -\frac{4000}{T} + 14.1$$

The heat of formation of the hydride was determined to be -7.95 kcal/ Mole H_2.

3. $CaNi_5$-H System

Activation occurred rapidly at room temperature and about 40 atm. The system is very stable up to $CaNi_5H_{1.8}$. Above this, a more unstable condition exists up to $CaNi_5H_5$. The hydrogen saturation achieved was $CaNi_5H_{5.7}$. The Van't Hoff relationship was as follows:

$$\ln p(\text{atm}) = -\frac{3430}{T} + 10.7$$

The heat of formation of the hydride was -6.82 kcal/mole H_2. Cursory studies were conducted to determine the poisoning effects with exposure to H_2S and 1% CO gas additions. The compound was relatively resistant to poisoning as denoted by degree of saturation of hydrogen and the desorption kinetics.

4. NiTi-H System

Activation of this system was extremely slow. Even at 425°C and 100 atm, the activation was slow. The saturation value of hydrogen at room temperature and about 100 atm was found to be $NiTiH_{1.3}$. A Van't Hoff plot was determined in the temperature range of 378 to 444°C to be:

$$\ln p(\text{atm}) = -\frac{10,100}{T} + 13.3$$

The heat of formation of the hydride is -20.1 kcal/mole H_2. These data were determined principally for purposes of correlation of AB compound properties.

5. CeMg-H System

This compound activated rapidly at room temperature and 7 atm. However, the hydride was too stable for the purposes of this study. The equilibrium pressure in the plateau region even at 300°C was about 0.02 atm. The saturation value was determined to be $CeMgH_{3.4}$. Attempts to obtain a Van't Hoff plot were thwarted by very slow kinetics.

6. RE Cu_5-H Systems

The heavy rare earth-Cu_5 systems were of interest because the interstitial hole sizes were comparable with $LaNi_5$. Thus, the $ErCu_5$, $GdCu_5$, and YCu_5 compounds were prepared. Metallography was conducted, and these alloys were not single-phase. The same alloys were prepared at ACu_4 stoichiometry., and single-phase conditions were exhibited. Although the literature[8] cites lattice parameters for the ACu_5 series, the compounds do not exist. The x-ray diffraction data had been mistakeningly interpreted as ACu_5 structures when they were ACu_4 structures. The ACu_4 alloys are of the $CaCu_5$ type of structure.

The $ErCu_4$ and $GdCu_4$ samples were subjected to activation at room temperature and 60 atm. Absorption occurred slowly. The saturation value obtained was approximately 0.8 H/ACu_4. This was too low to be of interest, so this series of studies was discontinued.

7. RE Fe_5-H Systems

The $REFe_5$ compounds with heavy rare earths were of interest because the interstitial hole sizes from available lattice parameter data were comparable to $LaNi_5$. Compounds of $GdFe_5$, $ErFe_5$, $GdFe_4$, and $ErFe_4$ were arc-melted. The same question about the existence of AFe_5 (or AFe_4)

compounds was raised as it was with ACu_5 compounds. Metallographic analysis indicated that both $GdFe_5$ and $ErFe_5$ were two-phase. The $GdFe_4$ and $ErFe_4$ alloys were also two-phase. Reference to the current investigations[9] indicates that neither the AFe_4 or AFe_5 compounds exist, but that A_6Fe_{23} (Th_6Mn_{23}) and A_2Fe_{17} (Th_2Ni_{17}) occur in this region

Since no AB_5 compounds of the $CaCu_5$ type exist with rare earth iron alloys, this series of systems was dropped from further studies.

8. $ZrBe_5$-H System

This compound could not be activated.

9. $(La-Ce)$ Ni_5-H System

The $La_{.4}Ce_{.6}Ni_5$ and $La_{.2}Ce_{.8}Ni_5$ alloys were of interest because they complete the studies undertaken by the Philips scientists[6]. Philips researchers were not able to hydride beyond $La_{.4}Ce_{.6}Ni_5$, because the pressures were becoming too high. Using an ultra-high pressure Sievert's, these alloys were hydrided successfully during this program. Pressures of 240 and 340 atm (3500 and 5000 psi) were required to acti-vate the two samples, respectively, at room temperature. It was noted that the amount of hysteresis between absorption and desorption was increasing rapidly with increasing Ce content. Also, the equilibrium desorption plateau pressure at a specific temperature was increasing with increasing Ce content. The alloys with $Ce_{0.6}$ and $Ce_{0.8}$ had 25°C desorption isotherm plateau pressures at 3H/M of 14 and 22 atm, respec-tively. The comparable absorption isotherm pressure plateaus were 37 and $\sim$68 atm, respectively. These alloy studies led obviously to the

investigation of $CeNi_5$, which had not been previously hydrided despite attempts by other investigators.

10. $CeNi_5$-H System

The $CeNi_5$ compound was expected to be very unstable as a hydride from the hole size-stability criterion. A specimen was ultimately activated, but it was necessary to employ pressures up to 680 atm and to reduce the temperature to -20°C. Once activated, the sample absorbed and desorbed readily. The total absorptivity at -15°C was almost the same as $LaNi_5$ with a value of 6.5 $H/CeNi_5$ at saturation. The plateau pressures at 3.0 $H/CeNi_5$ at -15°C on absorption and desorption were 21 and 110 atm, respectively. At 25°C, the absorption pressure was determined to be about 240 atm and the desorption pressure was 50 atm. The hysteresis was exceedingly large, which was to be expected from the trends seen in the $(La-Ce)Ni_5$ alloys. A family of four isotherms were delineated at -15, 5, 15, and 25°C in desorption. A van't Hoff relationship was plotted and found to be:

$$\ln p(atm) = \frac{1700}{T} + 9.5$$

The heat of formation of the hydride was determined to be -3.4 kcal/ mole H_2.

Obviously, the studies of this system led next to mischmetal (MM) Ni_5 alloys, because cerium content of $MMNi_5$ compounds was now suspect as the cause of much of the peculiar behavior of the $MMNi_5$-hydrides.

11. Mischmetal (MM)Ni_5-H Systems

Mischmetal is principally a mixture of light-rare-earth metals

that is derived and reduced from a natural mineral concentrate. The proportion of the rare earths in mischmetal remains essentially the same as in the mineral. Mischmetal is rather variable in its major composition and purity content depending on the mineral source and the processing techniques employed to extract the metal. Thus, it was felt essential to characterize the mischmetal used in this study as carefully as possible. Mischmetal was obtained from MolyCorp as a product of the mineral, basnaesite. The nominal rare-earth composition was provided by the supplier as 30.8 w/o La, 51.6 w/o Ce, 4.4 w/o Pr, and 13.2 w/o Nd. However, metallographic examination exhibited a structure that had several metallic phases and considerable non-metallic phase. Therefore, for the purposes of better control and characterization, it was decided to synthesize mischmetal from high-purity elemental components. The MolyCorp bastnaesite composition was duplicated to prepare a $MMNi_5$ compound. This sample required 100 atmospheres to activate and to approach saturation. The hydrogen compositions at 3.0 $H/MMNi_5$ and room temperature in absorption and desorption were 56 and 21 atm, respectively. Total saturation was slightly above 6.0 H/ $MMNi_5$ at room temperature and 300 atm. Van't Hoff relationships were obtained both on absorption and desorption at 3.0 $H/MMNi_5$ as follows:

$$\text{Absorption:} \quad \ln p(\text{atm}) = -\frac{1710}{T} + 9.29$$

$$\text{Desorption:} \quad \ln p(\text{atm}) = -\frac{2970}{T} + 13.7$$

From these data the heats of formation of the hydride were -3.40 kcal/ mole H_2 for absorption and -5.90 kcal/mole H_2 for desorption. This difference is attributed to the non-equilibrium conditions on the absorption cycle.

12. Cerium-Free, $MMNi_5$-H System

On the basis of the studies of the $(La-Ce)Ni_5$ alloys, the $CeNi_5$ compound, and the $MMNi_5$ alloy, it is obvious the cerium containing rare-earth-pentanickel compounds are inferior for most practical applications of metal hydrides because of the high pressures needed to charge them and the gross hysteresis between absorption and desorption. This problem diminishes the prospect for utilizing the relatively inexpensive, naturally occurring combination of rare earth metals (mischmetal) for the formation of rare-earth-pentanickel hydriding alloys.

It is logical to question what effect the removal of cerium would have on the hydriding properties of $MMNi_5$. Discussions with MolyCorp personnel concerning the problems in removing cerium from the basnaesite concentrate during processing indicated that it was relatively easy to do. They felt that they could produce a commercial cerium-free mischmetal with little cost increment over normally prepared mischmetal. This provided the incentive to inquire into the properties of hydrides of cerium-free, $MMNi_5$ alloys.

A synthetic cerium-free mischmetal was prepared to the same proportions as in the previous study, i.e., 63.7 w/o La, 27.2 w/o Nd, and 9.1 w/o Pr. This material in turn was arc melted to form a pentanickel alloy. This sample activated easily at room temperature and 40 atm. In this respect it was similar to $LaNi_5$. The alloy absorbed slightly more than 6 H/MM*Ni_5 at 25°C and 30 atm. The plateaus were straight and slightly sloping. Very little hysteresis was exhibited. The kinetics of reaction were rapid. The 25°C desorption plateau pressure was 4.4 atm at 3 H/MM*Ni_5; the absorption value was 5.2 atm.

MM* = cerium free, mischmetal

A Van't Hoff plot was made for this system. The relationship is:

$$\ln p(atm) = \frac{-3680}{T} + 13.8$$

The heat of formation of the hydride was computed to be -7.30 kcal/ moleH$_2$. The general hydriding characteristics and the prospective low cost of the material of this system indicate that, as a storage material, it has excellent commercial potential.

A publication is to be prepared shortly on the studies of the (La-Ce)Ni$_5$, the CeNi$_5$, the MMNi$_5$, and the cerium-free, MMNi$_5$ hydrides.

13. PrNi$_5$-H System

This system activated readily at 25°C and 100 atm. It was dis- covered that by accidental contamination of the system, two plateaus had developed. The leak was resealed but continued studies indicated the two plateaus were permanent. The kinetics of reaction were still rapid and the total capacity at the end of the second plateau was PrNi$_5$H$_{6.0}$. The plateau pressure change occurred sharply at 4 H/PrNi$_5$. The pressure at 3 H/PrNi$_5$ was 13.3 atm at 25°C on desorption. The pressure at 5 H/PrNi$_5$ was 32 atm at 25°C on desorption. The hysteresis was not serious; the absorption value at 3 H/PrNi$_5$ was 18.5 atm at 25°C.

It was found that an uncontaminated sample of PrNi$_5$ would not form the second plateau. Also, its saturation value was only slightly above 4 H/PrNi$_5$. This phenomenon is anomalous and will require more study.

14. NdNi$_5$-H System

The activation of the compound occurred readily at 25°C and 100

atm. Only one plateau occurred in this system compared to the PrNi$_5$-H system. It was of interest to note the saturation level which was slightly above 4 H/NdNi$_5$ at 25°C and 50 atm. The plateau pressure at 3 H/PrNi$_5$ on desorption was 14.9 atm. The hysteresis on absorption placed the pressure under the same conditions at 22 atm.

A Van't Hoff plot was produced which gave the following relationship:

$$\ln p(atm) = -\frac{3100}{T} + 13.1$$

The heat of formation of the hydride computed from this relationship was -6.16 kcal/mole H$_2$.

15. HoNi$_5$-H System

This system was of interest to assist in the hole size-stability correlation studies. However, the sample did not activate at 680 atmospheres and -20°C so the study was postponed pending modification of the ultra high pressure Sieverts apparatus.

16. YNi$_5$-H System

This system also could not be activated even employing the 680 atm ultra-high-pressure system and -20°C temperature.

17. HfNi-H System

Only a cursory investigation was made of this system. The HfNi compound is of the CrB structure type as is ThCo, a known hydride former. Consideration of the hole size-stability correlation indicated this would be a potential candidate. Pressure-temperature-composition

studies were not conducted but the saturation value was determined to be $HfNiH_{3.3}$. Additional studies will be conducted to characterize this system in future research.

VII.   DEVELOPMENT OF PREDICTIVE CRITERIA

Most of the effort during the last six months of the contract period was devoted to developing a basic understanding of the "unstable" compound hydrides. The AB_5 ($CaCu_5$) and AB ($CsCl$) systems were analyzed, and a quantitative criterion was established relating interstitial hole size of the intermetallic compound with the free energy of formation (stability) of the hydride at a specific temperature. It is felt that this formulation is a major contribution to the knowledge of these systems.

A complete description and presentation of this correlation and its justification is being submitted for publication in the Journal of the Less Common Metals.

VIII.   PUBLICATIONS AND REPORTS

The following reports were issued during the course of the contract:

1. Lundin, C. E., Sullivan, R. W., and Magee, C. B., "Solid-State Hydrogen Storage Materials of Application to Energy Needs", First Semi-Annual Technical Report, Denver Research Institute, University of Denver, AFOSR Contract No. F44620-74-C-0020 (ARPA Order 2552), April 1974.

2. Lundin, C. E. and Lynch, F. E., "Solid-State Hydrogen Storage Materials for Application to Energy Needs", First Annual Report, Denver Research Institute, University of Denver, AFOSR Contract No. F44620-74-C-0020 (ARPA Order 2552), January, 1975.

3. Lundin, C. E. and Lynch, F. E., "Solid-State Hydrogen Storage Materials for Application to Energy Needs", Second Semi-Annual Technical Report, Denver Research Institute, University of Denver, AFOSR Contract No. F44620-74-C-0020 (ARPA Order 2552), January 1975.

4. Lundin, C. E. and Lynch, F. E., "Solid-State Hydrogen Storage Materials for Application to Energy Needs", Final Technical Report, Denver Research Institute, University of Denver, AFOSR Contract No. F44620-74-C-0020 (ARPA Order 2552), August 1976.

5. Lundin, C. E. and R. W. Sullivan, "The Safety Characteristics of LaNi$_5$ Hydride", Proceedings of THEME Conference, March 1974, University of Miami, Florida.

6. Lundin, C. E. and Lynch, F. E. "A Detailed Analysis of the Hydriding Characteristics of LaNi$_5$", Proceedings of the 10th IECEC Conference, University of Delaware, Newark, Delaware, August 1975, Published by the Institute of Electrical and Electronics Engineers, Inc., Ref. Publication 75CH0983-7 TAB, N.Y., N.Y.

7. Lundin, C. E., Lynch, F. E., and Magee, C. B., "Some Useful
    Relationships Between the Physical and Thermodynamic Properties
    of Metal Hydrides", Proceedings of the 11th IECEC Conference,
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